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离舌橐吾中一新三萜皂甙——离舌橐吾甙 A

赵 昱[1] 田 军[1] 贾忠建[2] 孙汉董[1]*
([1] 中国科学院昆明植物研究所植物化学开放实验室, 昆明 650204)
([2] 兰州大学有机化学研究所, 兰州 730000)

LIGUVEITOSIDE A, A NEW TRITERPENOID SAPONIN FROM LIGULARIA VEITCHIANA

ZHAO Yu[1], TIAN Jun[1], JIA Zhong-Jian[2], SUN Han-Dong[1]*
([1]*Laborotary of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences,* Kunming 650204)
([2]*Institute of Organic Chemistry, Lanzhou University,* Lanzhou 730000)

关键词 离舌橐吾, 菊科, 三萜皂甙, 离舌橐吾甙 A, 离舌橐吾醇
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In our previous paper, we reported two new eremophilane derivatives from *Ligularia veitchiana* [1]. Further research to the polar section of this plant led to the isolation of a new triterpenoid saponin, named Liguveitoside A. Its structure was determined on the basis of the spectral and chemical methods.

Liguveitoside A (**1**) was obtained as colorless needles, with a m. p. at 220—221℃, from the n-BuOH soluble part of the EtOH extract of the plant. Comparison of the ^{13}C NMR spectrum of 1 with those of the reported saponins [2] revealed that Liguveitoside A was an oleanane-type monodesmoside. The molecular formula of 1 ($C_{36}H_{56}O_8$) was concluded from the peak at m / z 617 $[M+H]^+$ in the positive FAB mass spectrum, while its fragment ion peaks were exhibited at m / z 439 $[M-GlcUA]^+$ and 423 $[M-OGlcUA]^+$, suggested the presence of a glucuronic acid piece in the molecule. Acid hydrolysis of 1 gave glucuronic acid (detected by PC), and the aglycone (**2**).

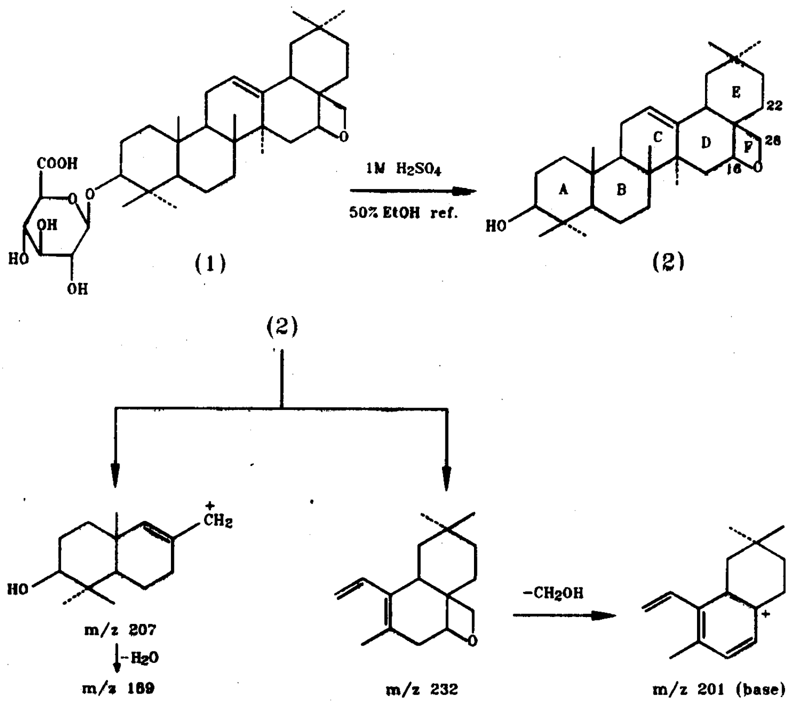
Compound 2 was analysed for seven tertiary methyls (δ0.73—1.16, 21H, 7 × Me), one $-CH_2O-$ group (an AB system at δ3.13 and 4.11, 1H each, a pair of doublets, J_{AB} = 10.8 Hz), one olefinic proton (δ5.13,t, J = 3.5 Hz) and two oxygen-bearing methine protons (δ3.17, dd, J = 10.0, 3.7 Hz; δ 4.24, ddd, J = 9.9, 2.4, 1.7 Hz).The EI mass spectrum of 2 showed a series of diagnostically important mass peaks at m / z 207, 189(207-H_2O), 232 and the base peak at m / z 201 (232-CH_2OH), which were typically attributed to a retro Diels-Alder fragmentation of an olean-12-en derivative bearing one hydroxy group in rings A / B [3].

Furthermore, a double doublet at δ3.17 in the ^1H NMR spectrum of 2 with coupling constants at J = 1.0 Hz (axial-axial coupling) and J = 3.7 Hz (axial-equitorial coupling) corresponded to 3α-H(axial

*通迅联系人 Author to whom correspondence should be addressed.

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proton), showed the equitorial orientation of the hydroxy group at C-3. According to the unsaturated value of **2**, another ring(named F ring) was most likely to exist in compound **2**. This ring was finally deduced to be a four-membered ring, formed by connection of C-28 and C-16 through an ether link. This could be evidenced by the ^{13}C NMR spectrum of **2**, for the chemical shifts of C-28 and C-16 was somewhat upfield shifted (by γ-effects each other) when comparing with the ^{13}C NMR spectra of the 16-hydroxy derivative and the 28-CH_2OH derivatives [4].



Moreover, one of the AB system protons (H-28) was found to be a double doublet (J = 10.8, 2.4Hz), while H-16 at δ4.24 exhibited as a ddd peak (J = 9.9, 3.7, 2.4Hz), suggested an long distance W-type coupling was present between H-16 and H-28. Shown by the demonstrating model, only an axial orientation of H-16 (16α-H) permits this W-type coupling.

In addition, no variation of C-14 and C-20 in the ^{13}C NMR spectrum of **2** was found when comparing with oleanane-type triterpenoids, also supported the above-mentioned structure.

Liguveitoside A (1): $C_{36}H_{56}O_8$, colorless needles, mp 220—221℃ (MeOH). FAB-MS(positive) (m / z): 617 $[M+H]^+$(36), 439(25), 423(87), 286(75), 273(100), 201(65), 176(84). ^{13}C NMR (δ, C5D5N): 38.90(C-1), 26.31(C-2), 89.11(C-3), 40.26(C-4), 55.83(C-5), 18.53(C-6), 34.37(C-7),41.11(C-8), 47.19(C-9), 36.86(C-10), 23.90(C-11), 122.66(C -12), 144.01(C-13), 43.96(C-14), 36.86(C-15), 66.80(C-16), 39.60(C-17), 44.62(C-18), 47.19(C-19), 31. 10(C-20), 33.05(C-21), 26.67(C-22), 28.25(C-23), 16.99(C-24), 15.70(C-25), 16.99(C-26), 27.17(C-27), 69.08(C-28), 33.41(C-29), 24.14(C-30); 107.20(C-1′), 77.80(C-2′), 78.22(C-3′), 73.44(C-4′), 75.59(C-5′), 172.75(C-6′).

Liguveitol (2): $C_{30}H_{48}O_2$, colorless gum, EIMS (m / z): 440$[M]^+$(92), 423(55), 232(57), 201(100). ^{13}C

NMR (δ,C_5D_5N): 38,63(C-1), 26.21(C-2), 78.73(C-3), 39.78(C-4), 55.22(C-5), 18.32(C-6), 33.58(C-7), 40.11(C-8),46.76(C-9), 38.77(C-10), 23.46(C-11), 122.30(C-12), 142.98(C-13), 43.67(C-14), 36.04(C-15), 67.52(C-16), 36.84(C-17), 44.72(C -18), 46.64(C-19), 30.73(C-20) ,32.56(C-21), 27.18(C-22), 28.08(C-23), 15.52(C-24,25),16.65(C-26), 26.76(C-27), 70.88(C-28), 33.06(C-29), 23.87(C-30).

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Δε253-1.02(MeOH; c 0.164)表示。

10. NMR 表示为^{1}H NMR 或^{13}C NMR, 须注明仪器的频率, 溶剂及内标物。化学位移以 δ 值(对TMS)表示, 注明峰形, 如: 单峰(s), 宽单峰(brs), 双峰(d), 双二重峰(dd), 复峰(m)等。^{13}C NMR 及^{1}H NMR 数所须注明所对应的碳和氢的位置, 采用 IUPAC 定位, 标为 C-1, C-2; H-1, H-2。例如: ^{13}C NMR(21.15Mz, $CDCl_3$): δ30.1(t, C-5), 74.1(d, C-6), 121.3(d, C-3), 144.2(s, C-4)。^{1}H NMR(100MHz, $CDCl_3$): δ0.681(3H, s, H-18), 0.884(6H, d, J=6.0Hz, H-26 and H-27), 0.901(3H, d, J=5.0Hz, H-21), 4.342(1H, q, J6α, 7α=4.5Hz, J6α, 7β=2.0Hz, H-6), 4.211(1H, m, $W_{1/2}$=18.0Hz, H-3α)。所用仪器频率及溶剂若在实验部分的总论中已注明, 则以下皆可省略。

11. 质谱须注明所用的方法, 如(EIMS, CIMS, GC-MS, FABMS 等)及离解能, 只须给出分子离子峰及重要的特征碎片峰(相对强度), 如:EIMS(70eV m/z(%): 386[M$^+$](36), 368[M-H_2O]$^+$(100), 275[M-111]$^+$(35) 等。高分辩质谱(HRMS)若有必要可多给一些信息。

12. 紫外光谱表示法, 如 UVλ_{max}^{EtOH}nm(lgε): 203(4.17)。

13. 红外光谱表示法, 如 IRν_{max}^{KBr}cm^{-1}: 1740。官能团的指定放在圆括号内, 如: 1740(>C=O)。若要标明吸收带的强度, 则采用以下缩写符号: w (弱), m (中等), v (可变), s (强), vs(很强)。

14. 有机化合物和无机化合物及有关的缩写符号须规范化(参考 CA), 如氘代溶剂 $CDCl_3$, DMSO-d_5, D_2O, pyridine-d_5 等。常见化学试剂在文中均以化学符号表示, 如: MeOH, EtOH, n-BuOH, PrOH, iso-PrOH, PhOH(苯酚), petrol (石油醚), $CHCl_3$, CCl_4, C_6C_6, Et_2O, Me_2CO, HOAc, EtOAc, THF, Ac_2O, NaOMe, CH_2N_2, HCO_2H(甲酸), TCA(三氯乙酸), TFA(三氟乙酸), NaOAc, NaOH, HCl, H_2SO_4, CO_2, H_3BO_3, NH_3, N_2 等。

15. 制备薄层析须注明(1) 薄层厚度; (2) 样品的量; (3) 确定带的方法; (4) 从吸附剂上洗脱下化合物所用的溶剂。特殊 TLC 的吸附剂须注明, 如: $AgNO_3$-硅胶(1∶9)。

16. 气相色谱 (GC)须注明检测器(FID,EC 等), 载气及流速, 操作温度, 柱子情况等。

17. 高压液相(HPLC) 须注明(1) 柱子情况, 如大小、型号; (2) 压力及溶剂; (3) 检测方法, 如 UV 或折射率。

18. X-衍射只须给出立体结构图(最好有键长)及必要的数据, 详细记录可指明在什么地方储存。